

# WHEN AND HOW IS SURFACE CHEMISTRY IMPORTANT IN WATER VAPOR ADSORPTION ON ACTIVE CARBONS?

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## Introduction

Water vapor adsorption on activated carbons has been studied extensively [1,2] but its understanding remains elusive [3,4]; it is difficult to separate the influences of carbon surface chemistry (e.g., the presence of surface functional groups) from those of carbon surface physics (i.e., pore size distribution).

Here we use microcalorimetry to illustrate the crucial role of surface chemistry, which is known to determine uptakes at low surface coverage, and we offer arguably novel insights into H<sub>2</sub>O adsorption on carbons.

## Experimental

A commercial activated carbon, Norit C (granular), prepared from a wood precursor by phosphoric acid activation (Nc), was used as the starting material (<70 mesh), after pretreatment in 5N HCl. It was subjected to a 950 °C heat treatment in either N<sub>2</sub> (N950) or H<sub>2</sub> (H950). The physical and chemical surface properties of the resulting carbons have been documented elsewhere [5]. A modified calorimeter was used to study the uptake of H<sub>2</sub>O at 70 °C [6].

## Results

Figures 1 and 2 summarize the results of the coverage dependence of H<sub>2</sub>O uptakes and adsorption heats. Surface chemistry modifications are seen to have dramatic effects on the character of H<sub>2</sub>O adsorption. As expected, the H<sub>2</sub>-treated sample adsorbed very little H<sub>2</sub>O, but the uptake is practically proportional to pressure. In contrast, on the as-received and N<sub>2</sub>-treated carbons, significant uptake increase occurs only beyond a threshold pressure ( $p/p_0$  of 0.3 for Nc and 0.6 for N950). It is also significant that at low pressures the uptake on N950 is larger than on Nc.

Dramatic changes are also evidenced by comparing the differential adsorption heats. Most of

the H<sub>2</sub>O on the as-received sample adsorbs with a heat slightly greater than 44 kJ/mol (heat of condensation of H<sub>2</sub>O). For N950 the heat is quite high at first and then it decreases very gradually until it too becomes similar to that of H<sub>2</sub>O condensation. The high-coverage heats on both samples are less than the heat of condensation. In contrast, for H950 there is virtually no uptake at heats close to that of H<sub>2</sub>O condensation: at very low coverage the heat is higher and subsequently it is lower than the heat of condensation. Exposure of H950 and N950 to O<sub>2</sub> at 150 °C (Figs. 3,4) has contrasting and significant effects as well. These are consistent with the carbon surface chemistry model presented earlier [5] and help to formulate the following model of H<sub>2</sub>O adsorption on carbons.

## Discussion

The results summarized here, together with the analysis of the relevant literature, suggest that there are three modes of H<sub>2</sub>O adsorption on carbon, and each can account for a significant fraction of the uptake. The importance of each type of adsorption observed on any particular carbon is clearly dependent on the carbon's surface chemistry.

First, there is chemical adsorption, with heats in excess of 50 kJ/mol, which occurs on free (unsaturated) carbon surface sites. Second, there is H<sub>2</sub>O condensation on the so-called "primary adsorption sites" (PAS), with heats of ca. 45 kJ/mol. Both the acidic, O-containing surface groups and the chemisorbed H<sub>2</sub>O molecules at graphene layer edges can act as PAS; the steep rise in the isotherm is a function of the number and character of these PAS, as well as of the pore structure. Third, there is physical adsorption, with heats of ca. 25 kJ/mol, which is due to weak dispersion interactions between H<sub>2</sub>O and hydrophobic carbon sites on the basal plane.

## Acknowledgment

Partial financial support from DOE (DE-FG22-95PC95225) is gratefully acknowledged.

## References

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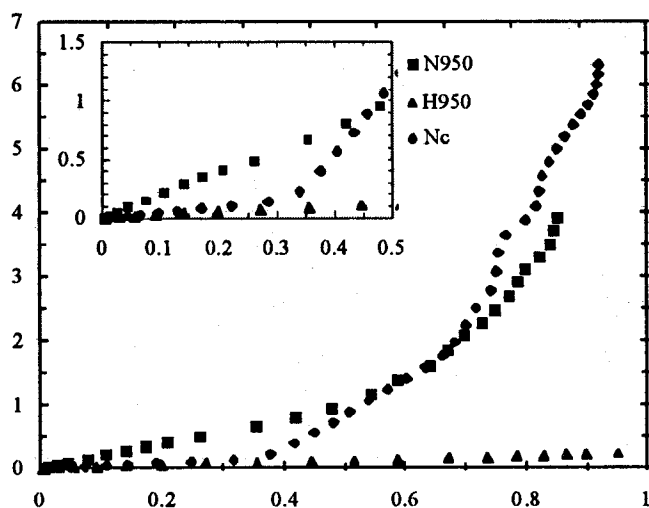


Figure 1. H<sub>2</sub>O adsorption (mmol/g) vs. relative pressure for the various carbons (at 70 °C).

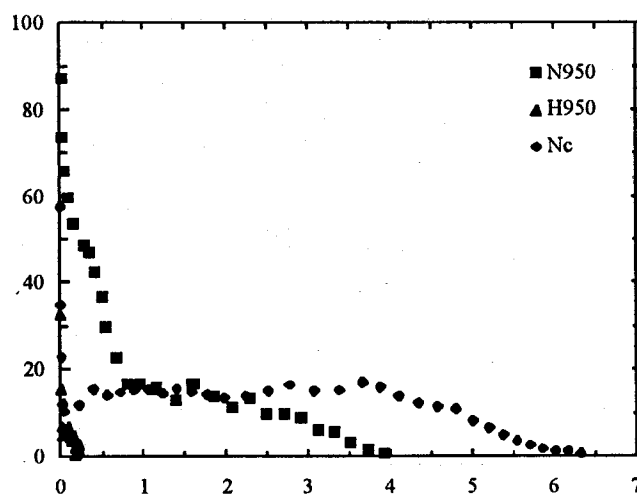


Figure 2. Heats of H<sub>2</sub>O adsorption (kcal/mol) vs. surface coverage (mmol/g) for the various carbons.

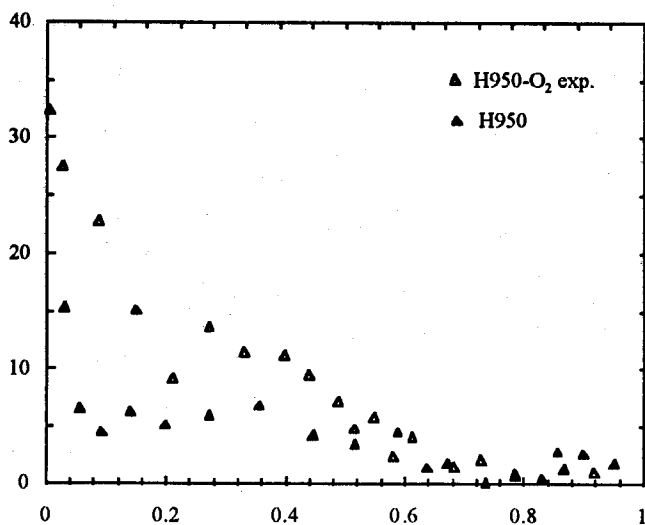


Figure 3. Heats of H<sub>2</sub>O adsorption (kcal/mol) vs. relative pressure for H950 and O<sub>2</sub>-treated H950.

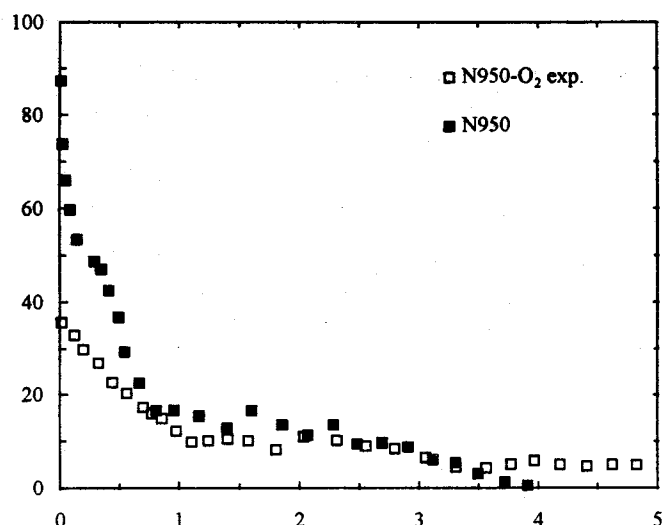


Figure 4. Heats of H<sub>2</sub>O adsorption (kcal/mol) vs. surface coverage (mmol/g) for N950 and O<sub>2</sub>-treated N950.